

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-230825  
 (43)Date of publication of application : 29.08.1995

(51)Int.Cl.

H01M 10/40

(21)Application number : 06-059729

(71)Applicant : JAPAN STORAGE BATTERY CO LTD

(22)Date of filing : 18.02.1994

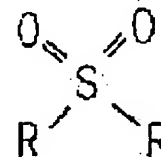
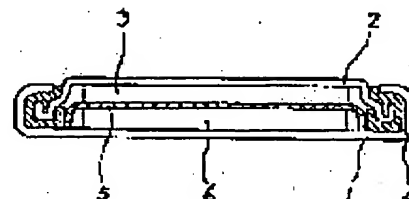
(72)Inventor : YOSHIDA HIROAKI

## (54) NONAQUEOUS ELECTROLYTE BATTERY

## (57)Abstract:

**PURPOSE:** To prevent deterioration of storage performance of a battery by using solvent including specific asymmetric and acyclic sulfone in the battery provided with a negative and a positive electrode, and nonaqueous electrolyte mainly comprising the solvent and solute.

**CONSTITUTION:** A battery comprises a separator of polypropylene in which organic electrolyte is impregnated, held by a positive electrode 6 mainly comprising lithium-cobalt composite oxide and a negative electrode 3 mainly comprising graphite, which are closed and sealed by a case 1 of stainless also acting as a positive electrode terminal and a sealing plate 2 of stainless also acting as a negative electrode terminal through a gasket 4. The electrolyte comprises solute such as lithium phosphate hexafluoride dissolved by solvent including asymmetric and acyclic sulfon expressed by a formula of ethylene carbonate, diethyl sulfone, etc., where in the formula, R is an alkyl group selected among ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, and t-butyl.



## LEGAL STATUS

[Date of request for examination] 31.10.1995

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 2734978

[Date of registration] 09.01.1998

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

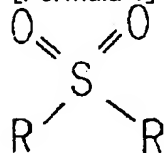
CLAIMS

---

[Claim(s)]

[Claim 1] The nonaqueous electrolyte cell which is a cell equipped with the nonaqueous electrolyte which makes a principal component a negative electrode, a positive electrode, and a solvent and a solute, and is characterized by containing the symmetry [ which is expressed with \*\* 1 ] un-annular [ the aforementioned solvent ] sulfone.

[Formula 1]



However, R is an alkyl group chosen from ethyl, n-propyl, an isopropyl, n-butyl, sec-butyl, an isobutyl, and t-butyl among \*\* 1.

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the lithium cell which is the high-energy density as the power supply for a drive or memory maintenance power supply of electronic equipment, and has high reliability.

[0002]

[Description of the Prior Art] With the formation of small lightweight with rapid electronic equipment, to the cell which is the power supply, it is small, lightweight, and high-energy density, and the demand to development of the rechargeable battery in which repeat charge and discharge are still more possible is increasing. As a rechargeable battery which fills these demands, a nonaqueous electrolyte rechargeable battery is the most promising.

[0003] Various things, such as lithium cobalt multiple oxides including 2 titanium sulfides, a spinel type lithium manganic acid ghost, a vanadium pentoxide, and a molybdenum trioxide, are examined by the positive active material of a nonaqueous electrolyte rechargeable battery. Especially, since [ more than 4V (Li/Li+) ] charge and discharge are extremely performed by electropositive potential, a lithium cobalt multiple oxide (LiCoO<sub>2</sub>) and a spinel type lithium manganic acid ghost (LiMn<sub>2</sub>O<sub>4</sub>) can realize the cell which has high discharge voltage by using as a positive electrode.

[0004] As for the negative-electrode active material of a nonaqueous electrolyte rechargeable battery, although various things, such as Li-aluminum alloys, carbon materials, etc. of a lithium including a metal lithium in which occlusion and discharge are possible, are examined, a carbon material has the advantage that a cell with a long cycle life with high and safety is obtained, especially.

[0005] However, in this seed cell, while making into a negative-electrode active material the lithium which has \*\*\*\* potential, in order to use the metallic oxide which has electropositive potential, it is in the situation that the electrolytic solution is easy to be decomposed in a negative electrode and each positive electrode in a positive electrode. Therefore, it is indispensable to consider as the composition which took these points into consideration in selection of the electrolytic solution, and using the various electrolytic solutions has been proposed. Those most mix hypoviscosity solvents, such as 1, 2-dimethoxyethane, dimethyl carbonate, ethyl methyl carbonate, and diethyl carbonate, as a solvent to high dielectric constant solvents, such as propylene carbonate, ethylene carbonate, gamma-butyrolactone, and a sulfolane.

[0006] On the other hand, generally as a solute; the lithium perchlorate, the trifluoromethane sulfonic-acid lithium, the 6 fluoride [ phosphoric acid ] lithium, etc. are used. A 6 fluoride [ phosphoric acid ] lithium is briskly used increasingly especially in recent years from the reason the ion conductivity of the electrolytic solution in which safety made it dissolve highly is high.

[0007] However, even if it used the electrolytic solution which was mentioned above, when the cell was stored at the elevated temperature for a long period of time, the electrolytic solution was decomposed in a negative electrode and each positive electrode, and there was a problem that a cell performance fell remarkably.

[0008]

[Means for Solving the Problem] this invention is a cell equipped with the nonaqueous electrolyte which makes a principal component a negative electrode, a positive electrode, and a solvent and a solute, and the above-mentioned problem is solved by containing the symmetry un-annular sulfone expressed with \*\* 1 by the aforementioned solvent.

[0009]

[Formula 1] However, R is an alkyl group chosen from ethyl, n-propyl, an isopropyl, n-butyl, sec-butyl, an isobutyl, and t-butyl among \*\* 1.

[0010]

[Function] As mentioned above, by this seed cell, it is easy to produce the decomposition reaction of the electrolytic solution, and it is possible that it is the main factor to which this degrades a cell performance. However, when the symmetry un-annular sulfone which has the alkyl group chosen as a solvent from ethyl, n-propyl, an isopropyl, n-butyl, sec-butyl, an isobutyl, and t-butyl was used, it excelled in the preservation property, and a cycle property also finds out that a good cell is obtained and came to complete this invention. That is, if the above-mentioned symmetry un-annular sulfone is used for the solvent of the electrolytic solution, since it is chemically stable in itself, it will be thought that a decomposition reaction stops being able to happen easily. Moreover, since it is chemically stable as compared with an unsymmetrical un-annular sulfone, a symmetry un-annular sulfone can offer the more excellent cell.

[0011]

[Example] Below, this invention is explained using a suitable example.

[0012] A positive electrode carries out pressurization molding, after mixing enough the carbon powder as a lithium cobalt multiple oxide ( $\text{LiCoO}_2$ ) and an electric conduction agent, and the fluororesin powder as a binder by the weight ratio of 90:3:7. A negative electrode carries out pressurization molding, after mixing a graphite and the fluororesin powder as a binder enough by the weight ratio of 91:9.

[0013] Drawing 1 is drawing of longitudinal section of a cell. It is the case which serves as the positive-electrode terminal which 1 pierced the stainless steel (SUS316) steel plate, and was processed in this drawing, and the obturation board which serves as the negative-electrode terminal into which 2 pierced the stainless steel (SUS316) steel plate, and it was processed, and the negative electrode 3 is contacted by the wall. The separator which consists of polypropylene into which 5 sank the organic electrolytic solution, and 6 are carrying out sealing obturation by binding tight the periphery of the obturation board 2 which serves as a negative-electrode terminal the opening edge of the case 1 which is a positive electrode and serves as a positive-electrode terminal through a caulking and a gasket 4 to the inner direction.

[0014] What dissolved the 6 fluoride [ phosphoric acid ] lithium in the organic solvent which mixed ethylene carbonate and the diethyl sulfone by the volume ratio 1:1 by the concentration of one mol/l. was used for the organic electrolytic solution. It did about 150microl pouring in of the above-mentioned electrolytic solution at the cell.

[0015] This cell size is 2mm in the diameter of 20mm, and height. And the cell created in this way was used as this invention cell (A).

[0016] Everything but having used the mixture (volume ratio 1:1) of ethylene carbonate and a dipropyl sulfone, the mixture (volume ratio 1:1) of a sulfolane and a diethyl sulfone, and the mixture (volume ratio 1:1) of a sulfolane and a dipropyl sulfone as an organic solvent set to (B), (C), and (D) the cell of this invention considered as the same composition as this example, respectively.

[0017] Everything but furthermore having used the mixture (volume ratio 1:1) of the mixture (volume ratio 1:1) of the mixture (volume ratio 1:1) of ethylene carbonate and ethyl methyl carbonate, ethylene carbonate, and 1 and 2-dimethoxyethane, the mixture (volume ratio 1:1) of a sulfolane and ethyl methyl carbonate and a sulfolane, and 1 and 2-dimethoxyethane as an organic solvent for comparison calls the comparison cell considered as the same composition as the cell of this invention a (a) (b), a (c), and (d), respectively.

[0018] Next, it is 10 cycle \*\*\*\*\* about the charge-and-discharge cycle-life examination which charges these cells by the 2.0mA constant current until terminal voltage results in 4.2V, and discharges until terminal voltage similarly amounts to 3V in a 2.0mA constant current. After stopping in the state of charge, it stored for ten days in 85-degree-C thermostat. 5 cycle deed cell capacity was checked for charge and discharge on the same conditions after storage and as storage before. The service capacity before storage of each cell (10 cycle eye) and after storage (5 cycle eye) is shown in Table 1.

[0019]

[Table 1]

|     | (A)     | (B)     | (C)     | (D)     |
|-----|---------|---------|---------|---------|
| 貯蔵前 | 27.5mAh | 27.1mAh | 26.8mAh | 26.4mAh |
| 貯蔵後 | 26.1mAh | 26.0mAh | 25.5mAh | 25.8mAh |

|     | (ア)     | (イ)     | (ウ)     | (エ)     |
|-----|---------|---------|---------|---------|
| 貯蔵前 | 28.3mAh | 26.8mAh | 27.9mAh | 26.9mAh |
| 貯蔵後 | 20.3mAh | 14.0mAh | 21.5mAh | 15.1mAh |

the Ming kana from the result of Table 1 -- like, although the cell capacity before storage was concerned with the kind of cell and was [ that there is nothing ] of the same grade, the cell capacity after storage had deteriorated about 50% about 30% in a comparison cell (a) and a (b) at a comparison cell (c) The fall of cell capacity of this invention cell (A), (B), and (C) is as small as about 5% or less, and it turns out that the outstanding keeping ability is shown.

[0020] In addition, although the above-mentioned example explained the case where a diethyl sulfone and a

dipropyl sulfone were used as an un-annular sulfone, the same effect will be acquired if the inside R of \*\* 1 is the un-annular sulfone which is the alkyl group chosen from ethyl, n-propyl, an isopropyl, n-butyl, sec-butyl, an isobutyl, and t-butyl.

[0021] As an example, a diisopropyl sulfone, a dibutyl sulfone, a diisobutyl sulfone, a G t-butyl sulfone, etc. are raised. Furthermore, in the above-mentioned example, although the case where a lithium cobalt multiple oxide was used as a positive active material was explained, various things, such as manganese dioxide including a lithium nickel multiple oxide ( $\text{LiNiO}_2$ ) and 2 titanium sulfides, a spinel type lithium manganic acid ghost ( $\text{LiMn}_2\text{O}_4$ ), a vanadium pentoxide, and a molybdenum trioxide, can be used. Moreover, although the graphite was used as a negative electrode, a negative-electrode active material can use the negative-electrode active material which is not limited fundamentally but is used for the conventional lithium cell, for example, a metal lithium, a lithium alloy, etc. in using the electrolytic solution of this invention. Moreover, in the above-mentioned example, although the example of application to a rechargeable battery was explained, the same effect is acquired also in a primary cell.

[0022] Moreover, a solute is not limited fundamentally, either. For example, one or more sorts, such as a lithium perchlorate, a 6 fluoride arsenic-acid lithium, 4 fluoride lithium borate, and a trifluoromethane sulfonic-acid lithium, can be used.

[0023] In addition, although each cell concerning the aforementioned example is a coin form cell, the same effect is acquired even if it applies this invention to a cylindrical shape, a square shape, or a paper form cell.

[0024] [Effect of the Invention] Being able to suppress effectively the fall of the keeping ability which is the problem of this seed cell by containing the symmetry un-annular sulfone which has the alkyl group as which the aforementioned solvent is chosen from ethyl, n-propyl, an isopropyl, n-butyl, sec-butyl, an isobutyl, and t-butyl in a cell equipped with the nonaqueous electrolyte which makes a principal component a negative electrode, a positive electrode, and a solvent and a solute, as mentioned above, the industrial value is size very much.

---

[Translation done.]

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**TECHNICAL FIELD**

---

[Industrial Application] this invention relates to the lithium cell which is the high-energy density as the power supply for a drive or memory maintenance power supply of electronic equipment, and has high reliability.

---

[Translation done.]

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**EFFECT OF THE INVENTION**

---

[Effect of the Invention] In the cell equipped with the nonaqueous electrolyte which makes a principal component a negative electrode, a positive electrode, and a solvent and a solute as mentioned above Being able to suppress effectively the fall of the keeping ability which is the problem of this seed cell by containing the symmetry un-annular sulfone which has the alkyl group as which the aforementioned solvent is chosen from ethyl, n-propyl, an isopropyl, n-butyl, sec-butyl, an isobutyl, and t-butyl, the industrial value is size very much.

---

[Translation done.]

---

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**TECHNICAL PROBLEM**

---

[Description of the Prior Art] With the formation of small lightweight with rapid electronic equipment, to the cell which is the power supply, it is small, lightweight, and high-energy density, and the demand to development of the rechargeable battery in which repeat charge and discharge are still more possible is increasing. As a rechargeable battery which fills these demands, a nonaqueous electrolyte rechargeable battery is the most promising.

[0003] Various things, such as lithium cobalt multiple oxides including 2 titanium sulfides, a spinel type lithium manganic acid ghost, a vanadium pentoxide, and a molybdenum trioxide, are examined by the positive active material of a nonaqueous electrolyte rechargeable battery. Especially, since [ more than 4V (Li/Li+) ] charge and discharge are extremely performed by electropositive potential, a lithium cobalt multiple oxide (LiCoO<sub>2</sub>) and a spinel type lithium manganic acid ghost (LiMn<sub>2</sub>O<sub>4</sub>) can realize the cell which has high discharge voltage by using as a positive electrode.

[0004] As for the negative-electrode active material of a nonaqueous electrolyte rechargeable battery, although various things, such as Li-aluminum alloys, carbon materials, etc. of a lithium including a metal lithium in which occlusion and discharge are possible, are examined, a carbon material has the advantage that a cell with a long cycle life with high and safety is obtained, especially.

[0005] However, in this seed cell, while making into a negative-electrode active material the lithium which has \*\*\*\* potential, in order to use the metallic oxide which has electropositive potential, it is in the situation that the electrolytic solution is easy to be decomposed in a negative electrode and each positive electrode in a positive electrode. Therefore, it is indispensable to consider as the composition which took these points into consideration in selection of the electrolytic solution, and using the various electrolytic solutions has been proposed. Those most mix hypoviscosity solvents, such as 1, 2-dimethoxyethane, dimethyl carbonate, ethyl methyl carbonate, and diethyl carbonate, as a solvent to high dielectric constant solvents, such as propylene carbonate, ethylene carbonate, gamma-butyrolactone, and a sulfolane.

[0006] On the other hand, generally as a solute, the lithium perchlorate, the trifluoromethane sulfonic-acid lithium, the 6 fluoride [ phosphoric acid ] lithium, etc. are used. A 6 fluoride [ phosphoric acid ] lithium is briskly used increasingly especially in recent years from the reason the ion conductivity of the electrolytic solution in which safety made it dissolve highly is high.

[0007] However, even if it used the electrolytic solution which was mentioned above, when the cell was stored at the elevated temperature for a long period of time, the electrolytic solution was decomposed in a negative electrode and each positive electrode, and there was a problem that a cell performance fell remarkably.

---

[Translation done.]



**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**MEANS**

[Means for Solving the Problem] this invention is a cell equipped with the nonaqueous electrolyte which makes a principal component a negative electrode, a positive electrode, and a solvent and a solute, and the above-mentioned problem is solved by containing the symmetry un-annular sulfone expressed with \*\* 1 by the aforementioned solvent.

[0009]

[Formula 1] However, R is an alkyl group chosen from ethyl, n-propyl, an isopropyl, n-butyl, sec-butyl, an isobutyl, and t-butyl among \*\* 1.

---

[Translation done.]

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**OPERATION**

---

[Function] As mentioned above, by this seed cell, it is easy to produce the decomposition reaction of the electrolytic solution, and it is possible that it is the main factor to which this degrades a cell performance. However, when the symmetry un-annular sulfone which has the alkyl group chosen as a solvent from ethyl, n-propyl, an isopropyl, n-butyl, sec-butyl, an isobutyl, and t-butyl was used, it excelled in the preservation property, and a cycle property also finds out that a good cell is obtained and came to complete this invention. That is, if the above-mentioned symmetry un-annular sulfone is used for the solvent of the electrolytic solution, since it is chemically stable in itself, it will be thought that a decomposition reaction stops being able to happen easily. Moreover, since it is chemically stable as compared with an unsymmetrical un-annular sulfone, a symmetry un-annular sulfone can offer the more excellent cell.

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## EXAMPLE

[Example] Below, this invention is explained using a suitable example.

[0012] A positive electrode carries out pressurization molding, after mixing enough the carbon powder as a lithium cobalt multiple oxide ( $\text{LiCoO}_2$ ) and an electric conduction agent, and the fluoro-resin powder as a binder by the weight ratio of 90:3:7. A negative electrode carries out pressurization molding, after mixing a graphite and the fluoro-resin powder as a binder enough by the weight ratio of 91:9.

[0013] Drawing 1 is drawing of longitudinal section of a cell. It is the case which serves as the positive-electrode terminal which 1 pierced the stainless steel (SUS316) steel plate, and was processed in this drawing, and the obturation board which serves as the negative-electrode terminal into which 2 pierced the stainless steel (SUS316) steel plate, and it was processed, and the negative electrode 3 is contacted by the wall. The separator which consists of polypropylene into which 5 sank the organic electrolytic solution, and 6 are carrying out sealing obturation by binding tight the periphery of the obturation board 2 which serves as a negative-electrode terminal the opening edge of the case 1 which is a positive electrode and serves as a positive-electrode terminal through a caulking and a gasket 4 to the inner direction.

[0014] What dissolved the 6-fluoride [ phosphoric acid ] lithium in the organic solvent which mixed ethylene carbonate and the diethyl sulfone by the volume ratio 1:1 by the concentration of one mol/l. was used for the organic electrolytic solution. It did about 150 microl pouring in of the above-mentioned electrolytic solution at the cell.

[0015] This cell size is 2mm in the diameter of 20mm, and height. And the cell created in this way was used as this invention cell (A).

[0016] Everything but having used the mixture (volume ratio 1:1) of ethylene carbonate and a dipropyl sulfone, the mixture (volume ratio 1:1) of a sulfolane and a diethyl sulfone, and the mixture (volume ratio 1:1) of a sulfolane and a dipropyl sulfone as an organic solvent set to (B), (C), and (D) the cell of this invention considered as the same composition as this example, respectively.

[0017] Everything but furthermore having used the mixture (volume ratio 1:1) of the mixture (volume ratio 1:1) of the mixture (volume ratio 1:1) of ethylene carbonate and ethyl methyl carbonate, ethylene carbonate, and 1 and 2-dimethoxyethane, the mixture (volume ratio 1:1) of a sulfolane and ethyl methyl carbonate and a sulfolane, and 1 and 2-dimethoxyethane as an organic solvent for comparison calls the comparison cell considered as the same composition as the cell of this invention a (a) (b), a (c), and (d), respectively.

[0018] Next, it is 10 cycle \*\*\*\*\* about the charge-and-discharge cycle-life examination which charges these cells by the 2.0mA constant current until terminal voltage results in 4.2V, and discharges until terminal voltage similarly amounts to 3V in a 2.0mA constant current. After stopping in the state of charge, it stored for ten days in 85-degree-C thermostat. 5 cycle deed cell capacity was checked for charge and discharge on the same conditions after storage and as storage before. The service capacity before storage of each cell (10 cycle eye) and after storage (5 cycle eye) is shown in Table 1.

[0019]

[Table 1]

|     | (A)     | (B)     | (C)     | (D)     |
|-----|---------|---------|---------|---------|
| 貯蔵前 | 27.5mAh | 27.1mAh | 26.8mAh | 26.4mAh |
| 貯蔵後 | 26.1mAh | 26.0mAh | 25.5mAh | 25.8mAh |

|     | (ア)     | (イ)     | (ウ)     | (エ)     |
|-----|---------|---------|---------|---------|
| 貯蔵前 | 28.3mAh | 26.8mAh | 27.9mAh | 26.9mAh |
| 貯蔵後 | 20.3mAh | 14.0mAh | 21.5mAh | 15.1mAh |

the Ming kana from the result of Table 1 — like, although the cell capacity before storage was concerned with the kind of cell and was [ that there is nothing ] of the same grade, the cell capacity after storage had deteriorated about 50% about 30% in a comparison cell (a) and a (b) at a comparison cell (c) The fall of cell capacity of this invention cell (A), (B), and (C) is as small as about 5% or less, and it turns out that the outstanding keeping ability is shown.

[0020] In addition, although the above-mentioned example explained the case where a diethyl sulfone and a dipropyl sulfone were used as an un-annular sulfone, the same effect will be acquired if the inside R of \*\* 1 is the un-annular sulfone which is the alkyl group chosen from ethyl, n-propyl, an isopropyl, n-butyl, sec-butyl, an isobutyl, and t-butyl.

[0021] As an example, a diisopropyl sulfone, a dibutyl sulfone, a diisobutyl sulfone, a G t-butyl sulfone, etc. are raised. Furthermore, in the above-mentioned example, although the case where a lithium cobalt multiple oxide was used as a positive active material was explained, various things, such as manganese dioxide including a lithium nickel multiple oxide (LiNiO<sub>2</sub>) and 2 titanium sulfides, a spinel type lithium manganic acid ghost (LiMn<sub>2</sub>O<sub>4</sub>), a vanadium pentoxide, and a molybdenum trioxide, can be used. Moreover, although the graphite was used as a negative electrode, a negative-electrode active material can use the negative-electrode active material which is not limited fundamentally but is used for the conventional lithium cell, for example, a metal lithium, a lithium alloy, etc. in using the electrolytic solution of this invention. Moreover, in the above-mentioned example, although the example of application to a rechargeable battery was explained, the same effect is acquired also in a primary cell.

[0022] Moreover, a solute is not limited fundamentally, either. For example, one or more sorts, such as a lithium perchlorate, a 6 fluoride arsenic-acid lithium, 4 fluoride lithium borate, and a trifluoromethane sulfonic-acid lithium, can be used.

[0023] In addition, although each cell concerning the aforementioned example is a coin form cell, the same effect is acquired even if it applies this invention to a cylindrical shape, a square shape, or a paper form cell.

---

[Translation done.]

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DESCRIPTION OF DRAWINGS**

---

[Brief Description of the Drawings]

[Drawing 1] It is drawing having shown the internal structure of the button cell which is an example of a nonaqueous electrolyte rechargeable battery.

[Description of Notations]

- 1 Cell Case
  - 2 Obturation Board
  - 3 Negative Electrode
  - 4 Gasket
  - 5 Separator
  - 6 Positive Electrode
- 

[Translation done.]

\*NOTICES\*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

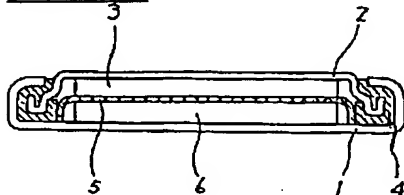
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

DRAWINGS

---

[Drawing 1]



---

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平7-230825

(43) 公開日 平成7年(1995)8月29日

(51) Int.Cl.<sup>6</sup>

H 0 1 M 10/40

識別記号

A

庁内整理番号

F I

技術表示箇所

審査請求 未請求 請求項の数1 書面 (全 4 頁)

(21) 出願番号

特願平6-59729

(22) 出願日

平成6年(1994)2月18日

(71) 出願人

000004282

日本電池株式会社

京都府京都市南区吉祥院西ノ庄猪之馬場町  
1番地

(72) 発明者

吉田 浩明

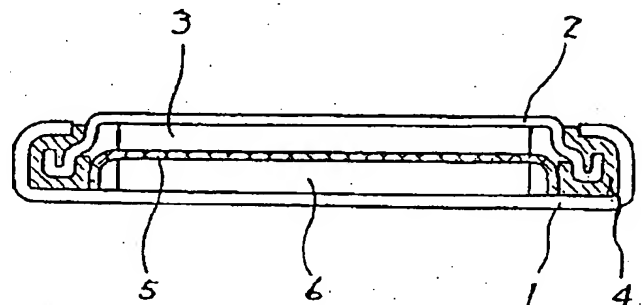
京都市南区吉祥院西ノ庄猪之馬場町1番地  
日本電池株式会社内

(54) 【発明の名称】 非水電解液電池

(57) 【要約】

【目的】 非水電解液電池の問題である貯蔵性能低下の防止を図る。

【構成】 負極と、正極と、溶媒と溶質とを主成分とする非水電解液とを備える電池において、前記溶媒がエチル、n-プロピル、イソプロピル、n-ブチル、sec-ブチル、イソブチル、t-ブチルから選ばれるアルキル基を有する対称非環状スルホンを含む。

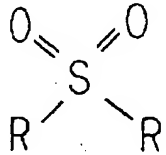


(2)

【特許請求の範囲】

【請求項1】 負極と、正極と、溶媒と溶質とを主成分とする非水電解液とを備える電池であって、前記溶媒が化1で表される対称非環状スルホンを含むことを特徴とする非水電解液電池。

【化1】



ただし、化1中、Rはエチル、n-プロピル、イソプロピル、n-ブチル、sec-ブチル、イソブチル、t-ブチルから選ばれるアルキル基である。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、電子機器の駆動用電源もしくはメモリ保持電源としての高エネルギー密度でかつ高い信頼性を有するリチウム電池に関するものである。

【0002】

【従来の技術とその課題】 電子機器の急激なる小形軽量化に伴い、その電源である電池に対して小形で軽量かつ高エネルギー密度で、更に繰り返し充放電が可能な二次電池の開発への要求が高まっている。これら要求を満たす二次電池として、非水電解液二次電池が最も有望である。

【0003】 非水電解液二次電池の正極活物質には、二硫化チタンをはじめとしてリチウムコバルト複合酸化物、スピネル型リチウムマンガン酸化物、五酸化バナジウムおよび三酸化モリブデンなどの種々のものが検討されている。なかでも、リチウムコバルト複合酸化物 ( $\text{LiCoO}_2$ ) およびスピネル型リチウムマンガン酸化物 ( $\text{LiMn}_2\text{O}_4$ ) は、4V ( $\text{Li}/\text{Li}^+$ ) 以上のきわめて貴な電位で充放電を行うため、正極として用いることで高い放電電圧を有する電池が実現できる。

【0004】 非水電解液二次電池の負極活物質は、金属リチウムをはじめとしてリチウムの吸蔵・放出が可能な  $\text{Li}-\text{Al}$  合金や炭素材料など種々のものが検討されているが、なかでも炭素材料は、安全性が高くかつサイクル寿命の長い電池が得られるという利点がある。

【0005】 しかし、この種電池において、卑な電位を有するリチウムを負極活物質とする一方、正極では貴な電位を有する金属酸化物を用いるため、負極、正極それぞれにおいて電解液が分解されやすい状況にある。従って、電解液の選択においてこれらの点を考慮した構成とすることが必要不可欠であり、種々の電解液を用いることが提案されてきた。それらの大部分は、溶媒としてプロピレンカーボネート、エチレンカーボネート、γ-ブチロラクトン、スルホランなどの高誘電率溶媒に1、2

ージメトキシエタン、ジメチルカーボネート、エチルメチルカーボネート、ジエチルカーボネートなどの低粘度溶媒を混合したものである。

【0006】 一方、溶質としては、過塩素酸リチウム、トリフルオロメタンスルホン酸リチウム、六フッ化リン酸リチウムなどが一般に用いられている。なかでも六フッ化リン酸リチウムは、安全性が高くかつ溶解させた電解液のイオン導電率が高いという理由から近年盛んに用いられるようになってきている。

10 【0007】 しかしながら上述したような電解液を用いても、高温で長期間電池を貯蔵すると負極、正極それぞれにおいて電解液が分解され、電池性能が著しく低下するという問題があった。

【0008】

【課題を解決するための手段】 本発明は、負極と、正極と、溶媒と溶質とを主成分とする非水電解液とを備える電池であって、前記溶媒に化1で表される対称非環状スルホンを含むことで上記問題を解決するものである。

20 【0009】

【化1】 ただし、化1中、Rはエチル、n-プロピル、イソプロピル、n-ブチル、sec-ブチル、イソブチル、t-ブチルから選ばれるアルキル基である。

【0010】

【作用】 前述した如く、この種電池では電解液の分解反応が生じやすく、これが電池性能を劣化させる主因となっていることが考えられる。しかしながら溶媒にエチル、n-プロピル、イソプロピル、n-ブチル、sec-ブチル、イソブチル、t-ブチルから選ばれるアルキル基を有する対称非環状スルホンを用いると、保存特性にすぐれ、サイクル特性も良好な電池が得られることを見出し、本発明を完成するに至った。すなわち電解液の溶媒に上記対称非環状スルホンを用いると、それ自体化学的に安定であるため分解反応が起こりにくくなると考えられる。また、対称非環状スルホンは、非対称の非環状スルホンに比較して化学的に安定であるため、より優れた電池を提供することができる。

【0011】

【実施例】 以下に、好適な実施例を用いて本発明を説明する。

【0012】 正極は、リチウムコバルト複合酸化物 ( $\text{LiCoO}_2$ ) と導電剤としてのカーボン粉末および結着剤としてのフッ素樹脂粉末とを90:3:7の重量比で十分混合したのち、加圧成型したものである。負極は、黒鉛と結着剤としてのフッ素樹脂粉末とを91:9の重量比で十分混合したのち、加圧成型したものである。

【0013】 図1は、電池の縦断面図である。この図において1は、ステンレス (SUS316) 鋼板を打ち抜き加工した正極端子を兼ねるケース、2はステンレス (SUSU316) 鋼板を打ち抜き加工した負極端子を



(3)

兼ねる封口板であり、その内壁には負極3が当接されている。5は有機電解液を含浸したポリプロピレンからなるセパレーター、6は正極であり正極端子を兼ねるケース1の開口端部を内方へかしめ、ガスケット4を介して負極端子を兼ねる封口板2の外周を締め付けることにより密閉封口している。

【0014】有機電解液にはエチレンカーボネートとジエチルスルホンとを体積比1:1で混合した有機溶媒に、六フッ化リン酸リチウムを1モル/リットルの濃度で溶解させたものを用いた。電池には、上記電解液を約1

50 $\mu$ l注液した。

【0015】この電池寸法は直径20mm、高さ2mmである。そして、このように作成した電池を本発明電池(A)とした。

【0016】有機溶媒としてエチレンカーボネートとジプロピルスルホンとの混合物(体積比1:1)、スルホランとジエチルスルホンとの混合物(体積比1:1)およびスルホランとジプロピルスルホンとの混合物(体積比1:1)を用いたことの他は本実施例と同様の構成とした本発明の電池をそれぞれ(B)、(C)および(D)とした。

【0017】さらに比較のために、有機溶媒としてエチレンカーボネートとエチルメチルカーボネートとの混合物(体積比1:1)、エチレンカーボネートと1,2-ジメトキシエタンとの混合物(体積比1:1)、スルホランとエチルメチルカーボネートとの混合物(体積比1:1)およびスルホランと1,2-ジメトキシエタンとの混合物(体積比1:1)を用いたことの他は、本発明の電池と同様の構成とした比較電池をそれぞれ(A)、(イ)、(ウ)および(エ)と呼ぶ。

【0018】次に、これらの電池を2.0mAの定電流で、端子電圧が4.2Vに至るまで充電して、同じく2.0mAの定電流で、端子電圧が3Vに達するまで放電する充放電サイクル寿命試験を10サイクルおこなった。充電状態で停止した後、85℃恒温槽中にて10日間貯蔵した。貯蔵後、貯蔵前と同様の条件で充放電を5サイクルおこない電池容量の確認をおこなった。各電池の貯蔵前(10サイクル目)および貯蔵後(5サイクル目)の放電容量を表1に示す。

【0019】

【表1】

4

|     | (A)     | (B)     | (C)     | (D)     |
|-----|---------|---------|---------|---------|
| 貯蔵前 | 27.5mAh | 27.1mAh | 26.8mAh | 26.4mAh |
| 貯蔵後 | 26.1mAh | 26.0mAh | 25.5mAh | 25.8mAh |

|     | (ア)     | (イ)     | (ウ)     | (エ)     |
|-----|---------|---------|---------|---------|
| 貯蔵前 | 28.3mAh | 26.8mAh | 27.9mAh | 26.9mAh |
| 貯蔵後 | 20.3mAh | 14.0mAh | 21.5mAh | 15.1mAh |

表1の結果から明かなように、貯蔵前の電池容量は電池の種類に関わりなく同程度であるが、貯蔵後の電池容量は比較電池(A)および(イ)で約30%、比較電池(ウ)では、約50%劣化していた。本発明電池(A)、(B)および(C)は電池容量の低下は約5%以下と小さく、優れた貯蔵性能を示すことがわかる。

【0020】なお、上記実施例では、非環状スルホンとしてジエチルスルホンおよびジプロピルスルホンを用いる場合を説明したが、化1中Rがエチル、n-プロピル、イソプロピル、n-ブチル、sec-ブチル、イソブチル、t-ブチルから選ばれるアルキル基である非環状スルホンであれば同様の効果が得られる。

【0021】一例として、ジイソプロピルスルホン、ジブチルスルホン、ジイソブチルスルホン、ジtert-ブチルスルホンなどがあげられる。さらに上記実施例では正極活物質としてリチウムコバルト複合酸化物を用いる場合を説明したが、リチウムニッケル複合酸化物(LiNiO<sub>2</sub>)、二硫化チタンをはじめとして二酸化マンガン、スピネル型リチウムマンガン酸化物(LiMn<sub>2</sub>O<sub>4</sub>)、五酸化バナジウムおよび三酸化モリブデンなどの種々のものを用いることができる。また、負極として黒鉛を用いたが、本発明の電解液を使用するにあたり、負極活物質は基本的に限定されず従来のリチウム電池に用いられている負極活物質、たとえば金属リチウム、リチウム合金などを用いることができる。また上記実施例では、二次電池への適用例を説明したが一次電池においても同様な効果が得られる。

【0022】また、溶質も基本的に限定されるものではない。たとえば、過塩素酸リチウム、六フッ化砒酸リチウム、四フッ化ホウ酸リチウム、トリフルオロメタンスルホン酸リチウムなどの1種以上を用いることができる。

(4)

5

【0023】なお、前記の実施例に係る電池はいずれもコイン形電池であるが、円筒形、角形またはペーパー形電池に本発明を適用しても同様の効果が得られる。

【0024】

【発明の効果】上述したごとく、負極と、正極と、溶媒と溶質とを主成分とする非水電解液とを備える電池において、前記溶媒がエチル、*n*-プロピル、イソプロピル、*n*-ブチル、*sec*-ブチル、イソブチル、*t*-ブチルから選ばれるアルキル基を有する対称非環状スルホン含有することで、この種電池の問題である貯蔵性能

は極めて大である。

【図面の簡単な説明】

【図1】非水電解液二次電池の一例であるボタン電池の内部構造を示した図である。

【符号の説明】

- 1 電池ケース
- 2 封口板
- 3 負極
- 4 ガスケット
- 5 セパレーター
- 6 正極

【図1】

